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FactSage and ChemApp: Two tools for the prediction of multiphase chemical equilibria in solutions^{*,**}

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Abstract: The integrated thermochemical databank system FactSage enables the user to calculate equilibria and thermodynamic properties for a wide variety of multicomponent, multiphase systems and reactions. The Gibbs energy models and databases for condensed, gaseous, and aqueous solutions presently implemented in FactSage are of interest to chemical and physical metallurgy, chemical and corrosion engineering, inorganic and solution chemistry, geochemistry, environmental science, etc. Models for the aqueous phase include the Pitzer and Helgeson formalisms, but data and subroutines for concentrated aqueous solutions have also been provided by OLI Systems. ChemApp is a programmer's library for thermochemistry that also incorporates the Gibbs energy minimizer of FactSage. Applications of ChemApp include, for example, the handling of repetitive complex equilibrium calculations in application-specific programs and its linking to third-party process simulation packages. In this work, user-defined aqueous solution models in FactSage and ChemApp have been applied to the hydrometallurgical processing of aluminum ores in both caustic and acidic leach solutions.

Keywords: chemical equilibrium calculations; thermochemical databases; aqueous solutions; user-defined solution models; Bayer process.

INTRODUCTION

Software for the prediction of chemical equilibria through Gibbs energy minimization and computerized thermochemical data are powerful tools in studying the chemistry of processes involving alloys, molten salts, oxides, aqueous solutions, and gases. FactSage [1] is an integrated thermochemical databank system consisting of a suite of information, database, and calculation modules. With the various modules, one can access and manipulate pure substance and solution databases, perform a wide variety of thermochemical calculations, including those of multiphase chemical equilibria, and generate tables, graphs, and figures of interest to chemical and physical metallurgists, chemical engineers, corrosion engineers, inorganic chemists, geochemists, ceramists, electrochemists, environmentalists, etc.

Around 20 Gibbs energy models for condensed solution phases are presently implemented in FactSage. Aqueous models include several variations of the Pitzer and Helgeson–Tanger–Shock for-

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malisms. In addition, data and subroutines for concentrated aqueous, organic, and non-ideal gaseous phases have also been provided as user-defined by OLI Systems [2].

The Gibbs energy minimizer of FactSage is also incorporated into ChemApp [3], a programmer's library for thermochemistry. Potential applications for the use of ChemApp are almost limitless and include development of application-specific programs, for example, to handle repetitive complex equilibrium calculations. Furthermore, ChemApp has been linked to third-party process simulation packages for modeling new or optimizing existing technical processes.

In this paper, the refining of alumina will be investigated by applying user-defined aqueous solution models in FactSage and ChemApp to hydrometallurgical leach processes involving both caustic and acidic liquors.

FactSage

FactSage [1] is an integrated thermodynamic databank system, running in a Windows environment, which provides tools for the administration of thermochemical data of inorganic substances, for the execution of thermodynamic application calculation, and for the generation of thermodynamic data from experimental information. Three modules incorporate the FactSage Gibbs energy minimizer. These are Equilib (thermodynamic application calculations), Phase Diagram (phase diagram calculations), and OptiSage (generation of thermodynamic data).

Equilib performs complex equilibrium calculations for multicomponent, multiphase systems using global conditions of elementary amounts, temperature, and total pressure as input. Global conditions can also be used as target variables after defining a target. The most frequently used targets are given values of an extensive property, the formation or disappearance of a target phase, the precipitation from a target phase or an equilibrium mole fraction or activity. Possible tasks for Equilib might be to calculate the temperature at which adiabatic conditions prevail, to calculate a mineral solubility in water, or to calculate how much HCl must be added to a system for it to reach a given pH. Other types of calculations are those for which all phase transitions within a given interval of the target variables temperature, total pressure, or input amounts are predicted.

The Phase Diagram module can calculate phase diagrams of the classical three types with the choice of two potential axes (temperature, pressure, chemical potential, partial pressure), one potential axis and one axis with extensive property ratios (mole fractions, weight fractions), or two axes with extensive property ratios. Input mole fraction expressions can be reformulated, which makes a redefinition from mole fraction to molality possible.

The OptiSage module generates thermodynamic data from experimental information. This enables the user to invert complex equilibrium calculations such that the results of the calculation are used to optimize the Gibbs energy data of the various phases of a chemical system be they stoichiometric pure substances or ideal or non-ideal solutions. The algorithm in OptiSage is based on the method originally described by Königsberger and Eriksson [4].

The solution models available with FactSage and ChemApp are listed in Table 1.

Table 1 Solution models in FactSage and ChemApp.

<i>Models for solid and liquid solutions with optional magnetic contributions</i>	
	Redlich–Kister–Muggianu polynomial model for substitutional solutions [5]
	Kohler–Toop polynomial model for substitutional solutions [6]
	Compound energy sublattice model [7]
	Species chemical-potential bond-energy sublattice model (ChemApp only) [8]
	Two-sublattice order/disorder model [9]
	Two-sublattice ionic liquid model [10]
	Two-sublattice equivalent fraction model (also as polynomial model) [6]
	Modified quasichemical model in the pair approximation with optional solutes when the model describes oxidic slags [11,12]
	Two-sublattice modified quasichemical model in the quadruplet approximation [13]
	Gaye–Kapoor–Frohberg cell model for slags [14]
	Unified interaction-parameter model for dilute condensed solutions [15]
<i>Models for aqueous solutions</i>	
	Pitzer or Helgeson without interaction parameters (with or without Davies, with Debye–Hückel (Helgeson)) [16–18]
	Pitzer with interaction parameters (with or without asymmetrical higher-order electrostatic mixing terms, with or without default values of the alpha parameter) [16]
	Helgeson with Pitzer parameters (with or without default values of the alpha parameter) [17]
	Brønsted–Guggenheim–Scatchard specific ion-interaction theory (SIT) (ChemApp only) [19]
<i>Models for gaseous/fluid phases</i>	
	C-H-O-S-N-Ar fluid model based on molecular dynamics [20]
	Virial equation with Tsonopoulos' second virial coefficient correlation [21]
<i>Models supplied by users</i>	
	Routines developed by OLI Systems for gas, concentrated aqueous and organic liquids (FactSage only) [2]
	Dilute Henrian constituents added to all solutions (user-defined) [22]
	One-sublattice solution models supplied by a ChemApp user

The FactSage databases for alloys, slags, and molten salts are the largest set of evaluated and optimized thermodynamic databases for inorganic systems in the world. The description of these databases, under development for over 25 years, is extensive, and the interested reader is referred to ref. [1]. There are three databases available for aqueous solutions, and these will be briefly described here.

OLI Systems [2] has developed commercial computer software and databases that simulate aqueous-based chemical systems and employ a predictive thermodynamic framework for calculating the physical and chemical properties of multiphase, aqueous-based systems. A family of software simulation tools that address a wide range of applications is provided—from rates of corrosion, oil, and gas well plugging, and wastewater treatment, to chemical processing plant operation and optimization, reactive separations, and environmental simulations. Dynamic-link libraries (DLLs) based on the StreamAnalyzer of OLI are available with FactSage. The OLI Public Database includes thermodynamic, transport, and physical properties for 79 inorganic elements (including actinides, heavy and precious metals) and their associated aqueous species, data for a non-ideal gas phase and many pure solid precipitates and data for over 3000 organics (including electrolytes, chelates, and organometallic species). The data are applicable within the following ranges: temperature, –50 to 300 °C; pressure, 0 to 1500 bar; and ionic strength, 0 to 30 molal. Other OLI databases (Corrosion, Low Temperature, and Geochemistry) are also available.

The Helgeson database contains infinite dilution properties taken from the GEOPIG-SUPCRT public database [17]. It includes data for 84 elements, 22 gaseous constituents, 1343 dilute aqueous constituents, and 192 pure condensed phases. The solution model incorporates the Helgeson equation of state for temperatures up to 350 °C and pressures up to 165 bar. There are three concentration-dependent versions: the ideal dilute solution model is valid up to approximately 0.001 molal and the models

incorporating the Debye–Hückel and Davies equations are valid up to approximately 0.02 and 0.5 molal, respectively.

A relatively small aqueous database with Pitzer parameters, strictly valid only at 25 °C, is also available. This contains parameters for 96 solutes taken from a survey of the literature until 1996 for 49 cations and 36 anions. There are totally 650 single-salt parameters and 64 interaction parameters for aqueous electrolyte mixtures.

ChemApp

ChemApp is a generalized thermodynamic subroutine library, based on the Gibbs energy minimizer of FactSage, which can be called from any process simulation program, user-written or commercially available, to calculate multicomponent chemical equilibria in systems containing a multitude of different types of phases.

A software interface must exhibit some desirable features. It has to be easily understood and used by the application programmer, and it has to be available in a form such that the programmer can use a language and a platform he or she finds convenient. In the course of a process simulation, the interface might be called to make a Gibbs energy minimization thousands of times, for instance, to calculate local equilibrium or boundary conditions. It thus has to be fast and reliable and must rarely fail to converge.

Essentially, only four programming steps are necessary to be able to predict a chemical equilibrium composition. The first mandatory steps involve initialization of the interface and reading a data file containing thermochemical data for the actual system. Before setting the conditions for the calculation, the programmer might want to ask for details on the chemical system, e.g., total number of phases or the index number of a phase constituent, or to define some phases as metastable. In the simplest case, setting the conditions for the calculation just means defining temperature, pressure, and input amounts. One of these quantities can also be used as a variable when defining targets (see description of Equilib above). In the fourth step, the equilibrium calculation is being executed and results are collected.

Several commercial process simulation packages involving ChemApp as a Gibbs energy minimization engine are available. For a comprehensive review, see Petersen and Hack [3].

NOTES ON THE METHOD USED FOR GIBBS ENERGY MINIMIZATION

Gibbs energy minimization techniques are characterized by the molar amounts of the species assumed to be present in the system being systematically altered from a set of initial values to those yielding the lowest total Gibbs energy at a specified temperature and pressure. A thorough description of the minimizer used in FactSage and ChemApp is given by Eriksson and Hack [23].

It is evident that the computing times required to arrive at a global Gibbs energy minimum are shorter the more accurate the initial values. In FactSage and ChemApp, an iterative procedure is used for estimation [24], whereby the set of the most stable pure condensed phases or mixture phase constituents for each system component is found. The phases or phase constituents included in the set must have compositions that are linearly independent, and all mass balances must be respected with non-negative amounts. To improve convergence, the final most stable set is internally chosen as new system components.

In the particular case when two consecutive input conditions are known to be similar, which is frequent during target or phase diagram calculations, it is more efficient to use the last computed equilibrium as starting estimate.

The total Gibbs energy for a phase at constant temperature (T) and pressure (P) can be expressed as

$$G = \sum n_i(g_i^\circ + RT \ln x_i + RT \ln \gamma_i) \quad (1)$$

where the summation is made over all constituents of the phase, n represents a molar amount, x a mole fraction, and R the gas constant. The standard molar Gibbs energy, g° , and the partial molar excess Gibbs energy, $RT \ln \gamma$, are in general temperature- and pressure-dependent and might also include magnetic contributions. For the gas phase, a term $RT \ln P$ would have to be added to eq. 1. Gibbs energies for aqueous phases are molality-dependent, which implies that a conversion factor $1000/[M(\text{H}_2\text{O})x(\text{H}_2\text{O})]$ has to be applied, where M denotes molar mass and the factor 1000 arises when the units of M are g mol^{-1} , whereas the units of molality are mol kg^{-1} . For pure condensed phases, x and γ are both equal to unity.

The Gibbs energies of the phases which have been estimated as the most stable are next summed up and the minimum of this function at constant temperature and pressure is to be achieved with the constraints imposed by the mass balance equations. When applying Lagrange's method of undetermined multipliers, equations are derived assuming ideal phase conditions whereas the chemical potentials themselves are replaced by their non-ideal values. This is an important approximation. Firstly, and most importantly, this approximation cancels out when a local or global minimum of the Gibbs energy surface is reached. Secondly, this feature enables a simple implementation of user-defined solution models since it makes the differentiation of the expressions for the partial excess Gibbs energy with respect to mole fraction redundant.

If the equilibrium phases predicted by the estimation routine lead to a local minimum or are such that the iteration process does not converge, phases have to be added or removed with corresponding modifications to the total Gibbs energy equation until the calculated minimum of the Gibbs energy surface corresponds to the global. The efficiency of this procedure is dependent on the quality of the starting estimate and the number of local minima calculated until the equilibrium phase assemblage is found.

USER-DEFINED SOLUTION MODELS

Three groups of user-defined solution models are permitted in ChemApp. One group applies to gaseous phases only and requires critical properties as input. The remaining two apply to condensed phases of the one-sublattice type. In these groups, of which the latter is not valid for aqueous solutions, contributions from a given interaction to the partial or integral excess Gibbs energy of all phase constituents are expected as output, respectively. In addition, to be able to calculate partial excess Gibbs energies also for models belonging to the third group, the partial derivative of the integral excess Gibbs energy with respect to the mole fraction of all phase constituents has to be provided.

Variables necessary to program an aqueous solution model are being transferred from the Gibbs energy minimizer of ChemApp through an argument list. These include temperature, total pressure, molality, and charge of all solutes, the parameter A_ϕ of the Debye–Hückel limiting law, the ionic strength, and the sum of solute molalities. The minimizer expects the following values to be returned: the contribution to the partial excess Gibbs energy from the Debye–Hückel term after this has been divided by a solute charge squared, to the partial excess Gibbs energy of all phase constituents from the given interaction, and to the osmotic coefficient from the Debye–Hückel term or from the given interaction.

Especially for aqueous solutions, a user might want to modify a model already available with ChemApp, for instance, when a temperature-dependent term of a Pitzer interaction parameter is not permitted in ChemApp, e.g., $RT/(T - T')$ or $RT/(T - T'')$, where T' and T'' are constant temperatures [25]. For several examples of this kind of user-defined models, see Königsberger et al. [26]. Other reasons for coding user-defined models included the use of specific equations of state for water and the ability to select between several (user-defined) Pitzer models without having to read more than one data file [26].

APPLICATIONS

Thermodynamic process simulation of a Bayer refinery circuit

The Bayer process is employed worldwide for the refining of alumina from bauxite ores. It involves hot, concentrated, alkaline sodium aluminate solutions (“Bayer liquors”) for the selective extraction of alumina (“digestion”) and, on cooling, the subsequent precipitation of purified gibbsite, $\text{Al}(\text{OH})_3$. Although the process is mature (it was patented by the Austrian chemist Karl Josef Bayer in 1888), ongoing technological improvements are needed to increase productivity and reduce energy consumption. Insights gained from a thermochemical simulation of the process can help to achieve these goals.

In a recent process simulation of the Bayer circuit [27], ChemApp was combined with a Bayer liquor model developed at Murdoch University [26]. The model is based on the Pitzer equations [28] and currently comprises 10 components (water plus sodium hydroxide, aluminate, carbonate, sulfate, chloride, fluoride, oxalate, formate, and acetate). It is capable of calculating, in a thermodynamically consistent manner, solution properties such as heat capacities, enthalpies, entropies, densities, water activities, activity coefficients, vapor pressures, and boiling-point elevations, together with solubilities of solid phases relevant to the Bayer process, over the wide temperature and concentration ranges of industrial interest.

A ChemApp-based FORTRAN code was specifically developed that simulates the liquor cycle of the Bayer process from digestion, clarification, precipitation, evaporation, and back to digestion, including flash cooling and heating steps. Assuming stable or metastable chemical equilibrium, this code calculates, through repetitive iterations, a steady state determined by the compositions of the input and output streams to each stage, including the associated energy balances.

This simulation not only covered temperature and concentration ranges from boehmite digestion to gibbsite precipitation, it also permitted exploration of boehmite precipitation as a potential energy-saving modification of the process. To simulate the final step of alumina production, a counter-current reactor model describing the calcination of gibbsite or boehmite in a circulating fluid bed furnace was coded.

Furthermore, the simulation was able to predict the accumulation and precipitation of undesirable impurities in various stages of the liquor circuit. It also identified possible reductions in the overall energy consumption of the Bayer process [27].

Acid routes in alumina refining

Many bauxite deposits are running out of economically attractive, low silica ore. In the Bayer process, digestion of bauxite with hot, concentrated alkaline aluminate solutions is preceded by a desilication step at $\sim 95^\circ\text{C}$, in which the “reactive” silica (e.g., kaolinite) contained in the ore forms insoluble sodium aluminosilicates that are discharged as part of the “red mud”, which contains primarily iron minerals that are insoluble in Bayer liquors. Since desilication implies losses of both sodium hydroxide and alumina, the Bayer process becomes uneconomical when the content of reactive silica in the ore exceeds a certain level.

In this regard, the use of sulfuric or hydrochloric acid is an important possibility—it is a well-known fact that acidic solutions leach aluminum minerals selectively from high-silica bauxites. The key issue of acid leaching is the relative solubility of the bauxite’s iron compounds such as hematite or goethite. Dealing effectively with iron contaminants underpins current and proposed methods for acidic processing of a number of base metals, especially regarding chloride-based leachates. In particular, mixtures of aqueous solutions of hydrochloric acid and magnesium chloride have been investigated in the development of high-concentration chloride leaching processes [29–31], in which the formation of chloro-complexes, the pronounced lowering of water activity and the associated increase in proton activity due to the presence of high Mg^{2+} levels are the key factors for the control of iron hydrolysis and precipitation [32].

The thermodynamic properties of mixed, concentrated aqueous solutions of hydrochloric acid and magnesium chloride, as well as the solubilities of aluminum and iron minerals therein, were calculated using the OLI Public and Geochemical Databases available with FactSage. All redox reactions were restricted in these calculations. The results for vapor pressures, boiling points, and solubilities of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in HCl – MgCl_2 solutions are very similar to those obtained from a Pitzer model developed recently [33]. Calculated solubilities of hematite, Fe_2O_3 , in these mixed solutions at elevated temperatures were close to measured data [34].

FactSage/OLI solubility calculations were also performed on mixtures of minerals resembling bauxite. The main components of bauxite comprise gibbsite ($\text{Al}(\text{OH})_3$) and/or boehmite (AlOOH) as the major source of aluminum, a variety of iron(III) minerals, silicates (including kaolinite, $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, which dissolves in caustic solution and forms part of the “reactive silica”) and a large range of minerals (containing Ti, P, Ca, F, V, etc.) that occur in minor and trace amounts. For the first set of calculations, a “bauxite” mixture containing gibbsite [equivalent to $w(\text{Al}_2\text{O}_3) = 70\%$], kaolinite [$w(\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}) = 20\%$], and hematite [$w(\text{Fe}_2\text{O}_3) = 10\%$] was selected.

Figure 1 shows the individual solubilities of these three minerals in aqueous HCl – MgCl_2 solutions at 100°C . It is noteworthy that kaolinite dissolves incongruently, i.e., Al dissolves and SiO_2 precipitates. While the individual solubility of gibbsite is virtually identical to its solubility in the “bauxite” mixture (see Fig. 1), the solubilities of hematite and kaolinite become suppressed when they dissolve together with gibbsite (Fig. 2). Under these circumstances, kaolinite dissolves congruently because of the high Al concentration in solution resulting from gibbsite dissolution.

A solubility simulation involving a “bauxite” mixture with minor impurities [$w(\text{Al}_2\text{O}_3) = 66.15\%$, $w(\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}) = 18.9\%$, $w(\text{Fe}_2\text{O}_3) = 9.45\%$, $w(\text{FeTiO}_3) = 3\%$, $w(\text{CaCO}_3) = 2\%$, $w(\text{CaF}_2) = 0.3\%$ and $w(\text{V}_2\text{O}_5) = 0.2\%$] indicates that the solubility of gibbsite is only slightly affected (Fig. 3). However, all minor impurities are predicted to dissolve completely which might limit the technical viability of alumina refining processes via acid routes.

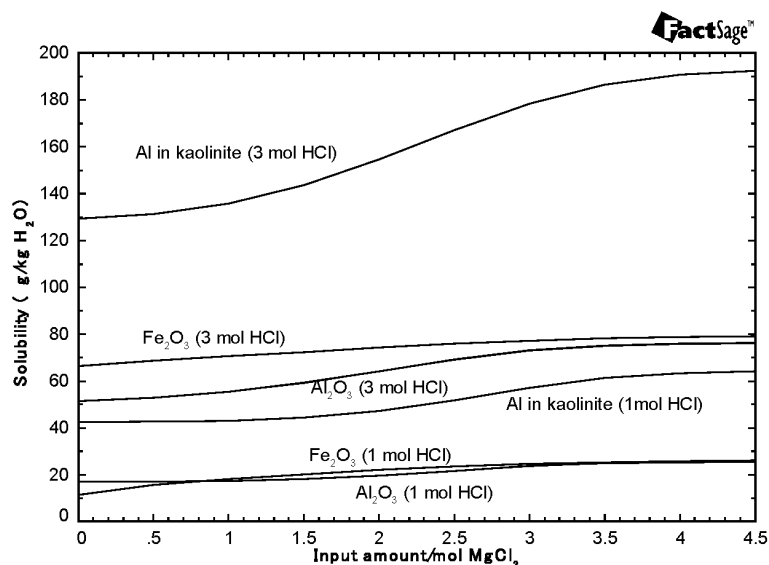


Fig. 1 Individual solubilities of $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, Fe_2O_3 , and $\text{Al}(\text{OH})_3$ in aqueous HCl – MgCl_2 solutions (containing 1 kg H_2O) at 100°C , as calculated by FactSage/OLI. The solubility of $\text{Al}(\text{OH})_3$ in a “bauxite” mixture [$w(\text{Al}_2\text{O}_3) = 70\%$, $w(\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}) = 20\%$, and $w(\text{Fe}_2\text{O}_3) = 10\%$] is virtually indistinguishable from its individual solubility. At high MgCl_2 concentrations, the OLI speciation model predicts AlOHCl^+ (rather than Al^{3+}) to be the predominant aqueous Al species, resulting in a ca. 1.5-fold increase in the solubilities of the Al minerals.

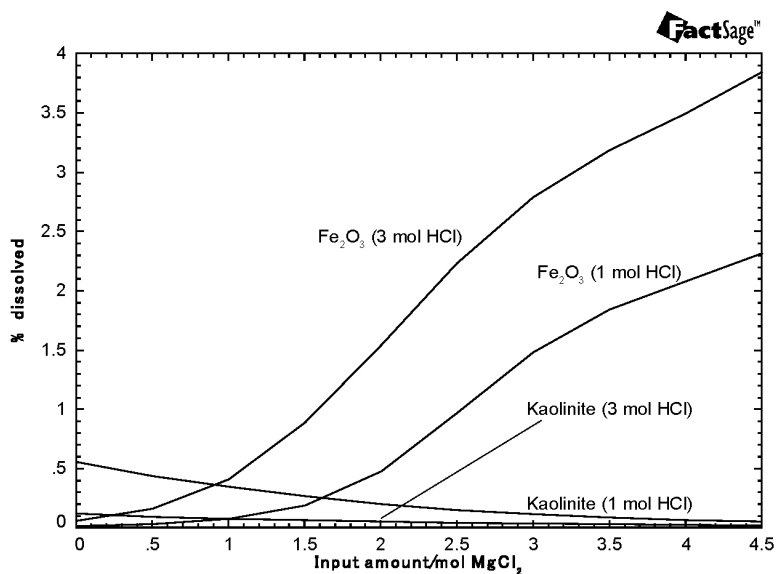


Fig. 2 Percentage of $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ and Fe_2O_3 dissolved when aqueous HCl – MgCl_2 solutions at 100°C are saturated with respect to $\text{Al}(\text{OH})_3$, as calculated by FactSage/OLI. Input: 1 kg H_2O and a “bauxite” mixture containing $w(\text{Al}_2\text{O}_3) = 70\%$, $w(\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}) = 20\%$, and $w(\text{Fe}_2\text{O}_3) = 10\%$.

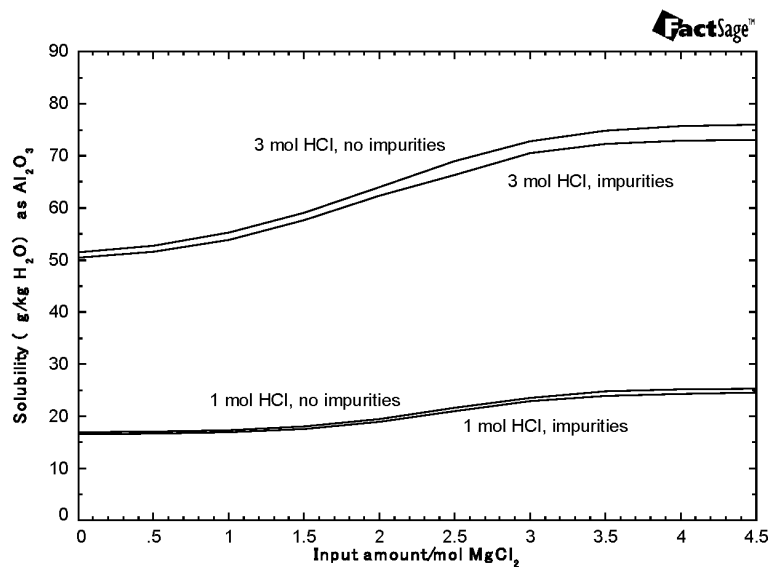


Fig. 3 Solubility of $\text{Al}(\text{OH})_3$ in aqueous HCl – MgCl_2 solutions (containing 1 kg H_2O) at 100°C , as calculated by FactSage/OLI. Minor impurities in “bauxite” (see text) slightly decrease the solubility of gibbsite, $\text{Al}(\text{OH})_3$.

CONCLUSIONS

FactSage and ChemApp are valuable tools for the study of solution chemistry when combined with “user-defined” models and critically evaluated databases for aqueous systems. Such models have been provided, e.g., by OLI Systems [2] for FactSage or by ChemApp users [26]. The software and models described in this study can be applied to the prediction of thermodynamic properties of hydrometallurgical liquors and thus to the optimization of existing and the development of new industrial processes.

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